



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) EP 0 457 822 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
20.03.1996 Bulletin 1996/12

(51) Int Cl. 6: **D21H 17/70, D21H 19/38**

(21) Application number: **90903246.8**

(86) International application number:
PCT/SE90/00037

(22) Date of filing: **16.01.1990**

(87) International publication number:
WO 90/09483 (23.08.1990 Gazette 1990/20)

(54) PAPER MANUFACTURING PROCESS, AND PAPERS OBTAINABLE BY MEANS OF THAT PROCESS

PAPIERHERSTELLUNG UND SO ERZEUGTES PAPIER

PROCEDE DE FABRICATION DE PAPIER, ET PAPIERS OBTENUS A L'AIDE DE CELUI-CI

(84) Designated Contracting States:
AT DE ES FR GB IT NL

- ÖSTENSSON, Per, Ove, Leo
S-892 00 Domsjö (SE)
- KUNI, Stefan, Olof
SF-48100 Kotka (FI)

(30) Priority: **13.02.1989 SE 8900475**

(74) Representative: **Barz, Peter, Dr. et al**
Patentanwalt
Kaiserplatz 2
D-80803 München (DE)

(43) Date of publication of application:
27.11.1991 Bulletin 1991/48

(56) References cited:

(73) Proprietor: **MO OCH DOMSJÖ AKTIEBOLAG**
S-891 91 Örnsköldsvik (SE)

- Paperi ja Puu, Vol. 9, 1976 DAN EKLUND: "The use of gypsum in pigment coating", see page 558 - page 570.
- Svensk papperstidning, Vol. 7, 1989 INGRID FINEMAN: "Morgondagens tryckpapper: Mera kortflber och mineral", see page 34 - page 39 page 39, third column.

(72) Inventors:
• ANDERSSON, Kjell, Rune
S-892 00 Domsjö (SE)

EP 0 457 822 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description**Technical field**

5 This invention relates to reusing/recycling gypsum-containing cellulose fiber material in the manufacture of paper from a pulp stock of pH >6.5. The invention provides a technical solution so as to eliminate problems involved with the production of coated papers using gypsum pigments. It is applicable to the manufacture of coated and non-coated grades of paper, both wood-free and wood-containing, having a basis weight of 15 g/m² or more and also comprising paperboard products. The invention provides a possibility of manufacturing gypsum-coated papers which have excellent 10 optical properties (brightness, whiteness, opacity, and light scattering coefficient).

15 The cellulose fiber materials used in this process are in the first place recycled broke and/or waste paper. The content of gypsum in the cellulose material, calculated as CaSO₄ without water of crystallization, usually exceeds 0.5% (w/w) and may be for instance more than 1% or 2% (w/w). As a rule the gypsum content is less than 60% (w/w) although in some cases it may amount to up to 70% (w/w).

State of the art

20 Within the field of papermaking systems, the reuse of cellulose fibers has been a time-honored classical expedient for minimizing the cost of raw materials. The procedure followed is to disintegrate either paper that has been used previously (so-called waste paper) or paper that has been produced recently and been rejected for being defective (broke), whereupon the resultant suspension is integrated into the stock employed for making the paper. The expression 25 that "the suspension is integrated into the stock" means that its dry matter material wholly or partly forms the stock so as to totally or partially constitute the dry matter material of the stock "solids". Disintegration is normally performed in an aqueous medium. Various procedures of and problems inherent in processing of broke and waste paper have been described earlier in for example US-A-3,865,684 and GB-A-9503. As regards the reuse of gypsum-containing cellulose fiber materials, there are no good methods available.

30 For a long time it has been known that gypsum may be used as a coating pigment in paper manufacturing techniques. See for example Eklund, D, Paperi ja Puu (1976) No. 9 pp. 559-70. Gypsum is a comparatively inexpensive material because it is obtained as a by-product in phosphate production processes and in systems for purifying SO₂-containing gases with lime.

35 For gypsum grades refined for paper manufacture see for instance EP-A-125,225, 125,224 and 112,317. It is believed that to obtain a high-quality coating on paper a gypsum pigment may typically have a particle size of <10 microns preferably <3 microns. The best pigments in the market are recrystallized (reprecipitated) materials, and have an F content and a P₂O₅ content of <0.3%. Calcium carbonate may be present in small amounts as an impurity. For further information see inter alia EP-A-112,317.

40 Calcium carbonate (CaCO₃) is frequently used as a filler. In nature, it occurs in the form of for instance chalk and calcite, and upon then having been subjected to grinding, it has been used in paper making processes. However, the form of calcium carbonate with which the best results have been obtained has been a synthetically produced, precipitated calcium carbonate (PCC); this is obtainable with a very homogeneous particle size distribution and in the form of uniform 45 crystals. The usual way of producing PCC is either to react milk of lime with carbon dioxide or to react an aqueous solution of calcium chloride with sodium carbonate. In both of these processes, controlled and well-defined conditions are required in order to obtain a PCC of suitable physical properties. But PCC may be an expensive material as compared to other fillers; consequently such other fillers have often been chosen instead. For a survey see Gill, R. and Scott, W., Tappi Journal, Jan. 1987, pp. 93-99.

Problems involved with the reuse of gypsum-containing cellulose fiber material

50 Papermakers hitherto have taken little interest in gypsum as a coating pigment. This is presumably due to the high water solubility of gypsum (2 g/l). In normal papermaking processes, some 10 to 40% of the production is usually rejected for reasons of quality and processing requirements, e.g. edge trimming. The rejected paper (broke) is disintegrated to form a 1-4% (w/w) solids suspension and is then reused in the process as fiber raw material. If this broke contains gypsum, a large portion thereof will be solubilized, because of the great solubility of gypsum - and if the worst comes to the worst this will give rise to a saturated solution of calcium sulfate. In view of the fact that the saturation concentration of calcium sulfate varies somewhat with temperature (maximum at about 40°C, CaSO₄ · 2H₂O), precipitates may be formed in process stages involving rapid changes in temperature, as e.g. in the press section and drying section of the paper machine. Such gypsum precipitates will form undesirable deposits on paper machine parts, thus causing poor runnability of the paper machine. In those cases where the calcium sulfate saturation concentration is not reached, calcium ions will accumulate anyway to high concentrations in the process water.

It is known, also, that calcium ions (Ca^{2+}) are adsorbed on the cellulose fiber surface thus reducing the swelling capacity and strength of the fiber; that is, in cases where high contents of Ca^{2+} are present the quality of the base paper produced will be deteriorated. A high concentration of Ca^{2+} in the papermaking process may also have a negative effect on the paper chemicals added, such as hydrophobicizing agents and flocculants.

If latex binding agents are present in the coating composition another problem may arise as a consequence of using water-soluble pigments such as gypsum: The gypsum is dissolved during the disintegration of the broke, so what then remains is a free latex binder, so-called "white pitch", which has a tendency to adhere to parts of the paper machine.

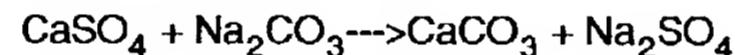
The invention provides a solution to these problems.

10 The invention

The technical solution proposed according to the invention for the manufacture of paper, using gypsum-containing cellulose fiber materials, is characterized by the features that carbonate ions and/or hydrogen carbonate ions are added to the aqueous medium in which the cellulose material has been or will be disintegrated, and that the pH is adjusted to above 7.3, with a preferred upper limit at pH 14, 50 that calcium carbonate is precipitated.

The thus resultant suspension is then passed on to the desired stock processing system where it may optionally be mixed with other cellulose pulps. In the stock processing system optional supplemental additives are added such as additional filler, retention aids, fluorescent whitening agents (= optical brightening agents) etc. There may thus be one or more further steps intercalated between the precipitation of CaCO_3 and the step where the suspension obtained is incorporated into the stock. According to an alternative embodiment of the process, calcium carbonate precipitation is effected by means of dosing CO_3^{2-} , HCO_3^- or CO_2 into the stock processing system. Finally the stock is spread onto a wire screen via the headbox of the paper machine; the paper is formed on the wire and drained, and then subjected to pressing and finally drying in the drying section of the machine. Thus in the paper as manufactured a precipitated calcium carbonate will be present as filler.

In the chemical literature it has very occasionally been reported that calcium sulfate is reacted with for instance sodium carbonate to commercially produce calcium carbonate.



The paucity of publications in this area is probably due to the circumstance that the reaction which takes place in the presence of solid CaSO_4 proceeds too slowly at high concentrations. It is quite surprising, therefore, that a practically complete carbonation of gypsum can be obtained from broke/recycled fibers under conditions such as are normally prevalent when this broke is being disintegrated. It is also very surprising that the process results in a narrow particle size distribution of small calcium carbonate particles having a mean size below 10 microns, such as 0.3-5 microns, and in the form of homogeneous crystals. Due to this last-mentioned feature the resultant precipitated calcium carbonate (PCC) can be used as a substitute for commercial PCC of the highest grade, with the added advantage that the paper-maker can readily produce this material in the normal processing system.

It appears that the present process results in the formation of substantially rhombohedral calcite (>50%), but presumably if different conditions are chosen other crystal forms are precipitated such as scalenohedral calcite, vaterite and aragonite.

It has also been observed that gypsum-coated paper is very easily disintegrated when the carbonation process is employed.

High-yield pulps such as are used in the manufacture of wood-containing coated papers are generally bleached without any addition of chlorine. The combination of PCC as the filler and gypsum as the coating pigment provides a way of producing an environmentally satisfactory paper, which has a much higher degree of brightness than the coated wood-containing papers manufactured by means of prior art techniques.

When bright and white wood-free coated papers are to be produced, i.e. papers from essentially chemical pulps, it is necessary, if current prior art techniques are applied to use fluorescent whitening agents, for example derivatives of stilbenesulfonic acid triazine. But for some years now the use of these optical whiteners has been called into doubt as being a potential health hazard; and in Italy for instance the use of such whitening agents is entirely prohibited in all kinds of packaging materials for foods, e.g. coated cardboard materials for foodstuff packaging.

This combination of PCC as filler and gypsum as coating pigment provides the possibility of substantially increasing whiteness and brightness in the paper, thus the demand for using the aforesaid whitening agents can be reduced or entirely eliminated in/from the manufacture of these paper products. The said combination is particularly suitable for brightness degrees of >80% ISO.

Various embodiments of the invention are defined in greater detail below and are summarized in the attached claims.

The carbonate ions/hydrogen carbonate ions used according to the invention may be added to the aqueous medium

prior to, after, or together with the cellulose fiber material. What really matters is to make sure that gypsum carbonation proceeds until the desired stage is reached, such that 5-100%, e.g. more than 50%, with a preferred range of 80-100%, of the gypsum in the cellulose material has been converted to calcium carbonate. The degree of carbonation is calculable from the added amounts of gypsum and carbonate ion/hydrogen carbonate ion. The addition of carbonate ions/hydrogen carbonate ions to the aqueous medium may be performed in one of several different ways. According to one alternative a water-soluble metal carbonate salt or ammonium carbonate salt or the corresponding hydrogen carbonate is added in a dissolved or solid state. Another alternative procedure involves generating the ions *in situ*, for example by first adding a suitable soluble metal hydroxide and then supplying carbon dioxide. If carbonate generation with carbon dioxide is employed it is necessary to keep the pH under close control since carbon dioxide has the effect of lowering the pH so that there is a risk of the pH becoming too low for the carbonation process. A soluble hydrogen carbonate behaves in fundamentally the same manner as a carbonate but is a less efficient reagent; this is due to the fact that its aqueous solutions are less alkaline and for that reason have much lower contents of carbonate ions. This can be compensated for by the addition of bases of the type where the pK_a of the corresponding acid is higher than or approximately equal to the pK_a of HCO_3^- , for example hydroxide ions.

Provided the pH is properly adjusted the same results may be obtained according to the invention using either soluble carbonate salt, soluble hydrogen carbonate salt or generating the carbonate *in situ*. These variant forms of the invention should therefore be regarded as being equivalent.

The terms "water-soluble carbonate salt" and "water-soluble hydrogen carbonate salt" are to be construed in the sense that the solubility properties of these salts are such that if an aqueous solution of such a salt has an stoichiometric (= equivalent) amount of gypsum added to it then this will cause calcium carbonate to be precipitated. In the normal case this means that the carbonate/hydrogen carbonate salts in question have a solubility (mol/lit.) exceeding that of calcium carbonate by a power of 10 as measured at the process temperature for the $CaCO_3$ precipitation. Examples of salts fulfilling these characteristics are alkali metal and ammonium carbonates, and the corresponding hydrogen carbonates.

The amount of carbonate salt to be added is calculated on the basis of the amount of added cellulose fiber material and the gypsum content thereof. Expressed as a percent of the stoichiometric amount for carbonation of the gypsum content of the added cellulose fiber material, the dose of soluble carbonate to be added should be within the range of 5-300%, the preferred range being about 80-200%. Both in the case of carbonate and in the case of hydrogen carbonate it is an important requirement that the pH be maintained within an optimum range for $CaCO_3$ precipitation, this being >

$(pK_{HCO_3^-} \text{ minus } 3)$, preferable > $(pK_{HCO_3^-} \text{ minus } 2)$. At 25°C, these values correspond to pH >7.3 and >8.3 respectively.

A preferred upper limit is pH = $(pK_{HCO_3^-} \text{ plus } 4)$, that is, pH = 14.3 at 25°C. In case the pH is found to lie outside these ranges at some point in time its readjustment is effected with acid or base, with the compensatory expedient of running the process for a longer time. If the pH goes down to below pH = pK_a of H_2CO_3 this will result in carbon dioxide evolution, to the effect that carbonate is removed. This may be compensated for by means of adding more CO_3^{2-}/HCO_3^- . The term

$pK_{HCO_3^-}$ refers to values measured at the processing temperature for the precipitation of $CaCO_3$. If conditions become too alkaline this may be deleterious to the cellulose fiber (yellowing).

Conversion of the gypsum content of the cellulose fiber material to calcium carbonate may be performed within a wide range of temperatures, of from 5 to 100°C. The preferred range is 10-70°C. Reaction times may vary from about one minute to a couple of hours.

The most practical application of the process according to the invention involves continuously dosing the gypsum containing cellulose fiber material, the water-soluble carbonate/hydrogen carbonate, and optional pH-adjusting chemicals into a disintegrator containing the aqueous medium. The process can be controlled by continuous measurement of the dissolved Ca^{2+} and the pH in the aqueous medium (i.e. in the disintegrator tank); if the pH rises after an optimum pH has been set this will indicate that there is an excess of soluble carbonate, whereas an increasing Ca^{2+} concentration and decreasing pH indicate that the added amount of soluble carbonate (including hydrogen carbonate) has been insufficient. Thus if there is a rise in the pH one will proceed by decreasing the amount of soluble carbonate added, or alternatively increasing the added amount of gypsum-containing cellulose fiber material; when the Ca^{2+} concentration increases or the pH becomes lower than the optimum value that had been set one will proceed by decreasing the added amount of cellulose fiber material or alternatively increasing the added amount of soluble carbonate.

The optical properties of paper produced according to the invention appear to depend on the repulping conditions. In our laboratory experiments, it seems that the best optical properties of the paper are obtained if the carbonate/hydrogen carbonate ions are dosed continuously or in small portions during the repulping of the gypsum containing broke.

5 The process of the invention gives a readily soluble sulfate as a by-product, e.g. sodium sulfate. In contrast to calcium sulfate these other sulfates are rather harmless entities in the papermaking process. It is however possible to reduce the amount thereof in the resultant pulp suspension, if necessary; viz., by means of filtration, ultrafiltration, reverse osmosis etc. The salt-rich water separated may then be passed on to the ordinary effluent treatment system of the paper mill.

10 According to one embodiment of the invention the paper produced (= the base paper) is coated with a coating colour preferably containing gypsum as its pigment component. Known grades of gypsum for coating purposes may be employed, as well as future grades. The composition of the coating colour is such as is common practice in this field - the coating colour containing in addition to pigment optionally also the following components; water, binder e.g. latex binder, starch, carboxymethyl cellulose and additives such as wet strength agents, fluorescent whitening agents, slimicides, and so forth. Latex binders are aqueous dispersions of small particles of a water-insoluble polymer. These polymer 15 particles which may consist of styrene butadiene rubber, polyacrylate, polyvinyl acetate etc. typically have a relatively low glass transition temperature (<50°C). The dry solids content of the coating colour is within the ordinary range as usually employed within this technical field, id est 5 - 80% (w/w), with the gypsum being 10-100% thereof. Binder forms part of the solids content and is normally set forth with reference to the total amount of pigment. The normal content of 20 binder calculated in this manner is 5-20% (w/w). The amount of coating applied is such as is normal in the present field of technology, i.e. 4-30 g/m² of the solids content of the coating colour. This embodiment of the invention is very practical, since paper broke formed in the process can be reused directly in the base paper manufacture. This embodiment comprises monolayer coating and multilayer coating, and coating on either one side or both sides of the paper. In each individual layer a different coating colour composition may be used.

25 On the filing date, the most preferred embodiment of the invention comprised precipitation of CaCO₃ with an alkali metal carbonate at 10-70°C, said alkali metal carbonate (preferably Na₂CO₃) being employed in an equivalent amount ($\pm 20\%$) relative to the gypsum, or in excess thereof. An embodiment equally preferred uses the same dosage of the corresponding hydrogen carbonate, and generation of carbonate in situ. An optimum pH here is the same as aforesaid.

30 One embodiment of the invention comprises a coated paper which contains filler in the base paper and contains pigment in a coating layer. The characteristic feature here is that the filler is partly or entirely a precipitated calcium carbonate (PCC), preferably 0.5-50% (w/w) of the weight of the paper, and that the pigment consists entirely or partly 35 of gypsum. The lower range of PCC contents (0.5-10% w/w) may apply to liner and paperboard products. For other paper products the PCC content amounts to 2-50% (w/w), in some cases down to as far as 0.5% (w/w) of the weight of the paper. Fluorescent whitening agents content may be lower than those commonly employed and may for example amount to <0.2% (w/w). Gypsum as a coating pigment may be incorporated in amounts such as are ordinary with conventional techniques; cp. above.

40 According to a preferred embodiment 5-100% (w/w) of the filler in the base paper (e.g. 5-50% w/w or 50-100% w/w) consists of precipitated calcium carbonate (PCC), and 5-100% (w/w) of the pigment in the coating layer (e.g. more than 50% w/w like for instance more than 90% w/w or about 100% w/w) consist of gypsum. The remaining ingredients may be other chemicals such as are commonly employed in papermaking processes (see above). The gypsum percentages and PCC percentages as set forth are calculated as percentages of the total content of mineral pigment and mineral 45 filler respectively.

45 The paper according to the invention may contain more than one filler. Thus it is possible to have clay, ground calcium carbonate, titanium dioxide etc. present therein together with the PCC. The paper also may contain a plurality of different coating pigments; these pigments being applied either as an admixture with one another or each in a separate layer.

The various types of paper according to the invention comprise different grades of coated paper such as coated fine paper, LWC and MWC grades, and coated paperboard, folding box board and liner.

50 As will be appreciated from the above information, one way of producing the paper according to the invention is that set forth in the attached claims. It is also possible to produce the paper according to the invention by starting from paper having a PCC filler and coating it with a gypsum-containing coating colour. If broke from the process is recycled, a carbonation of gypsum according to the above description will provide substantial advantages in this case, both practical and economical.

55 By using the inventive concept of employing recycled broke as a gypsum-containing cellulose material for the manufacture of gypsum-coated paper the base paper is supplied with PCC as a filler. If the recycled broke comprises 5-40% of the total fiber raw material the PCC thus supplied to the base paper will as a rule amount to 5-60% (w/w) of the filler in the paper produced. Depending on the amount of filler in the base paper and on the proportion of broke therein the proportional amount of PCC formed in the process may rise considerably higher (60-100% w/w).

Moreover it has been shown by means of electron microscopic studies that the method of this invention offers the

possibility to carbonate gypsum directly without being dissolved out of the binder of the coating layer. A new matrix is formed by PCC and binder. In cases where the coating layer contains latex binder and the coated paper is reused, this means that there is little tendency for the latex binder to be released in the form of "white pitch".

Because the process of the invention may result in a new matrix of PCC and the latex binder, a paper manufactured in accordance with the process of the invention may contain latex binder of the aforesaid type, for example in the form of such a matrix bound PCC in proportions as mentioned above.

The invention will now be illustrated by way of a number of examples which are non-limitative.

Example 1

10

A base paper produced on a commercial paper machine, basis weight 76 g/m², filler 17% (ground chalk), which had been given a surface sizing of oxidized starch containing fluorescent whitening agent (about 0.2% w/w on a dry paper basis, Blankophor P from Bayer, Germany), and which had been produced from fully bleached chemical pulps (sulfate pine: sulfate birch = 40:60) was coated by means of a laboratory coater (Dixon, Model No. 160 MK II/B) with a coating colour containing 59.7% solids; the composition of this coating colour being 100 parts of gypsum [PCS-91, (= reprecipitated, recrystallized) gypsum from Boliden Kemi, Sweden], 10 parts of latex binder (Dow 685, Dow Chemical Europe, Switzerland) and 1 part of carboxymethyl cellulose (CMC 7ELC1, Hercules Inc., USA). The coating colour was applied by way of a two-step procedure to thus produce a total coating weight of 55 g/m² dry coating layer on one side of the base paper.

20

Then pulp suspensions with 3% solids contents were produced from the gypsum-coated paper, both (i) in a conventional manner and (ii) in a manner according to the present invention. 60 g of paper were introduced into 2 liters of water in a disintegrator where the paper was then repulped for 15 minutes at 23°C. In the experiments representing tests of the invention 0.037 g, 0.074 g, 0.148 g and 0.233 g of Na₂CO₃ (Na₂CO₃ · 10 H₂O, Riedel-de Haen AG, Germany) per g of coated paper were added to the water immediately before addition of the paper.

25

After the disintegration of the coated paper a minor portion of each pulp suspension was set aside to be assayed, by means of atomic absorption, to determine the concentration of dissolved Ca²⁺.

30

Then 233 g of the pulp suspensions were diluted to 1 liter, the concentration thus becoming 0.7%. Of this suspension 414 g were charged into a Finnish sheet former (F 101) for handsheet production. After having been dewatered on the wire the sheets were subjected to pressing at 3.55 kg/cm² pressure, whereupon they were dried at 23°C and RH 50% for 24 hours. Basis weights and filler contents of the resultant sheets were determined (incineration in a furnace at 500°C). The optical properties brightness (ISO%), opacity and light scattering coefficient (557 nm) were also determined, with an Elrepho 2000. It should be mentioned also that these measurements were made in accordance with SCAN-P:75R, SCAN-P 8:75R and SCAN-C 27R-76.

The results obtained are set forth in Table 1.

35

Table 1

	Conv. paper sheet	Paper sheets produced acc. to the invention				
		A	B	C	D	E
40	Na ₂ CO ₃ (g/g coated paper)	0	0.037	0.074	0.148	0.233
	Basis weight (g/m ²)	67.7	71.2	70.6	70.2	68.3
	Dissolved Ca ²⁺ in pulp susp. (mg/l)	584	525	465	404	8
	Filler (%)	25.7	29.3	27.6	28.8	31.9
45	Brightness, ISO %	81.3	82.6	83.0	84.0	84.1
	Opacity %	86.1	88.3	89.4	90.4	89.5
	Light scattering coeff. (m ² /kg)	41.8	47.0	51.1	56.9	55.7

50

The results obtained show unambiguously that the process of the invention has highly positive effects on the optical properties of the paper sheets. Note also that the filler content of the sheets is significantly higher and that the content of dissolved Ca²⁺ has decreased dramatically in the pulp suspension due to the treatment with sodium carbonate.

In the manufacturing procedure of sheet E in Table 1, approximately a stoichiometrical amount of sodium carbonate has been added to the gypsum in the disintegrated coated paper. The filler in this sheet was studied by means of scanning electron microscope (SEM) and compared with a sheet that had been produced in a conventional manner.

55

The images obtained showed

- (1) that in the untreated sheet the filler contained gypsum particles of varying shapes and sizes, and
- (2) that the paper sheet manufactured according to the invention contained large amounts of precipitated calcium

carbonate in the form of rhombohedral calcite, with a very narrow particle size distribution (about 1 micron).

Energy dispersive X-ray analysis of a sheet produced according to the invention and a sheet produced in a conventional manner has shown

(1) that the sheet produced in the conventional manner has a high content of sulfur (from CaSO_4), and
 (2) that the sheet produced according to the invention is substantially sulfur-free, i.e. due to the carbonate treatment the gypsum from the coated paper has reacted to form calcium carbonate.

10 Example 2

In these tests, the same base paper was coated with the same coating colour as in Example 1. The coating operation was carried out in one step by means of the laboratory coater; the total amount applied was 23.5 g/m^2 dry coating layer on the base paper. Pulp suspensions were prepared in a way similar to that described in the preceding example, but this time the following water-soluble carbonates were tested: 0.17 g potassium carbonate (E. Merck AG, Germany) and 0.10 g sodium hydrogen carbonate (E. Merck AG) per gram of coated paper. Additions of the carbonates were made in the same way as before. This series of experiments also comprised a supplemental experiment with sodium hydrogen carbonate, with 1.2 ml of 1 M NaOH solution per gram of coated paper being added to the water prior to the addition of hydrogen carbonate. The intention here was to demonstrate that a certain degree of alkalinity is required in the system for obtaining the full effect of the sodium hydrogen carbonate.

The concentration of dissolved Ca^{2+} was determined in the pulp suspensions. Sheets of paper were manufactured in the same manner as described before. In the case of the experiments with sodium hydrogen carbonate, the pH was determined immediately before and after disintegration of the coated paper. The paper sheets produced were then analyzed with respect to their basis weight, filler content and optical properties in the same manner as in the preceding example. The results obtained from these experiments are set forth in Table 2.

Table 2

	Conv. paper sheet	Paper sheets produced acc. to the invention			
		A	B	C	D
	K_2CO_3 (g/g coated paper)	0	0.17	0	0
	NaHCO_3 (g/g coated paper)	0	0	0.10	0.10
	1M NaOH (ml/g coated paper)	0	0	0	1.2
35	pH before defibr.	5.8	-	8.1	11.1
	pH after defibr.	6.3	-	7.6	8.7
	Dissolved Ca^{2+} in pulp susp. (mg/l)	592	18	418	104
	Basis weight (g/m^2)	73.7	76.1	74.1	76.2
	Filler (%)	16.3	19.9	15.6	20.0
40	Brightness ISO %	82.1	85.7	83.1	85.8
	Opacity %	88.1	89.5	87.7	89.7
	Light scattering coeff. (m^2/kg)	44.0	53.1	44.6	53.9

These results show that very good effects have been obtained both with potassium carbonate and with sodium hydrogen carbonate. In the latter case, however, some alkali has to be added for attaining a fully satisfactory effect.

Example 3

These experiments were directed to evaluating the effect of added ammonium carbonate (J.T. Baker Chemicals BV, Holland) in repulped gypsum-coated paper. The coated paper carried a total of 6.5 g/m^2 dry coating layer on one of its sides. As for the rest the base paper, coating colour, disintegration and paper sheet production were the same as in Example 1. Dissolved Ca^{2+} concentration, basis weight, filler content and optical properties were determined in the sheets in the same manner as in the foregoing examples. Table 3 sets forth the results obtained in these tests.

Table 3

	Conventional paper sheets	Paper sheets produced acc. to the invention
5 (NH ₄) ₂ CO ₃ (g/g coated paper)	0	0.04
Dissolved Ca ²⁺ in susp. (mg/l)	496	261
Basis weight (g/m ²)	91.6	89.5
Filler (%)	18.6	20.3
10 Brightness ISO %	83.5	83.7
Opacity %	90.9	91.3
Light scattering coeff. (m ² /kg)	44.7	47.3

15 This experiments shows that significant positive effects are obtainable with small amounts of added ammonium carbonate.

Example 4

20 The gypsum-coated paper described in Example 1 was repulped in a conventional manner so as to form a 3% pulp suspension. This was mixed with a bleached pine sulfate pulp (2.3%) beaten to 24°SR, as follows:

25 Stock (a) 0.3 parts by weight of gypsum paper suspension (dry basis) + 0.7 parts by weight of pine sulfate pulp (dry basis).
Stock (b) 0.3 parts by weight of gypsum paper suspension (dry basis) + 0.7 parts by weight of pine sulfate pulp (dry basis) containing 0.155 g of Na₂CO₃/g pulp (dry basis).

In case (b) the sodium carbonate was added to the pine sulfate pulp before the incorporation of the gypsum paper suspension.

30 The paper stocks thus obtained were left to stand, with agitation, for about 15 minutes. Then sheets of paper were manufactured as described in Example 1. Basis weight, filler content, brightness (ISO%), opacity and light scattering coefficient of the paper sheets obtained were determined in accordance with methods as described earlier.

The results of these tests will appear from Table 4.

Table 4

	Paper sheets from stock (a)	Paper sheets from stock (b) (acc. to the inv.)
35 Basis weight	96.8	99.3
Filler (%)	4.2	6.2
Brightness, ISO %	81.6	82.8
40 Opacity %	84.0	86.4
Light scattering coeff.m ² /kg	31.1	36.0

These results show that good effects are obtainable also if carbonation is carried out after the broke from the gypsum-coated paper has been mixed with other stock-components.

Example 5

45 In this example coating tests were performed on paper sheets A and E which had been produced in accordance with the process described in Example 1. Sheet A produced in a conventional manner and sheet E treated with 0.233 g of Na₂CO₃/g of paper - so that precipitated calcium carbonate (PCC) was formed and constituted part of the filler content of the sheet - were coated manually with two different coating colours, the coating operation being performed with a manual blade applicator. One of the two coating colours was identical with the gypsum formulation described in Example 1 whereas the other coating colour was a conventional clay/chalk formulation which contained 60% solids having the following composition: 70 parts clay (SPS, ECC, England), 30 parts chalk (Hydrocarb 90 M, Omya, Germany), 10 parts latex binder (Dow 685, Dow Chemical Europe, Switzerland), 1 part carboxymethyl cellulose (CMC 7ELCI, Hercules Inc., USA), and 0.25 part dispersing agent (Polysalz, BASF AG, Germany).

55 Application of each coating colour (12-13 g of colour [calculated as solids] per m² of paper) was effected by means of a single coating operation on one side of each of sheets A and E. The sheets were dried for two minutes at 105°C

whereupon the optical properties were determined, *viz.* brightness (ISO%), whiteness CIE (W), light scattering coefficient (at 557 nm) and opacity (at basis weight 80 g/m²); these determinations being made with an Elepho 2000 and in conformity with the SCAN methods as set forth in Example 1. Whiteness CIE (W) is a European standard which is correlated with whiteness as experienced by the human eye. Table 5 sets forth the results obtained.

5

Table 5

Base paper	Sheet A (without PCC)		Sheet E (with PCC)	
Coating pigment	Clay/chalk	Gypsum	Clay/chalk	Gypsum
Brightness, ISO%	82.8	84.5	84.4	86.1
Whiteness, (CIE, W)	81.2	89.0	82.6	94.6
Light scattering coeff. (m ² /kg)	66.0	66.6	77.2	77.9
Opacity %, (80 g/m ²)	94.1	92.3	94.9	94.8

15

These results show that a coated paper with the combination of PCC as a base paper filler and gypsum as coating pigment will have much better optical properties than will coated papers manufactured with other combinations of filler + pigment in their base papers and coating layers respectively.

Base sheets A and E in this example contain fluorescent whitening agent from the machine-produced paper broke (see Example 1). Although fluorescent whitener does have an effect on the whiteness of the paper, it should be noted that the supplemental effect on whiteness as obtained by means of the PCC + the gypsum combination in our tests is extraordinarily great; that is, it appears that a synergism effect is obtained from the PCC filler and the gypsum pigment. This example shows that when the combination PCC + gypsum is employed, the papermaking process can be performed with lesser or zero amounts of fluorescent whitening agent.

25

Example 6

In this example, coating experiments were carried out on two base papers (fine papers) having a basis weight of about 70 g/m² and produced as follows:

30

(a) This base paper was manufactured on an experimental paper machine (width 220 mm, speed 1-2 m/min). The pulp composition was 40/60 fully bleached pine sulfate/birch sulfate, and the filler used was a chalk (DX 50, Omya, Germany). The filler content was 15.3%, and the paper was given a surface sizing of oxidized potato starch (about 1.5% on a dry paper basis).

35

Other additives such as retention aids, stock hydrophobicizing agents and cationic starch were of ordinary types such as are commonly used in the art of manufacturing fine paper.

40

(b) This base paper was produced with a precipitated calcium carbonate of the scalenohedral calcite type (Albacar HO, Pfizer Inc., USA). The filler content in this case amounted to 16.2%; as for the rest, conditions in the manufacturing procedure were the same as in A.

The two base papers A and B were blade-coated manually on one side with the gypsum formulation described in Example 1 (the amount applied being 12 g/m²).

45

Optical properties were determined as in the preceding examples, on (i) the uncoated base papers and (ii) the papers that had been coated. Results of these measurements are listed in Table 6.

Table 6

	Base sheet		Gypsum coated paper	
	A (chalk)	B (PCC)	A (Chalk)	B (PCC)
Brightness, ISO %	83.2	89.1	87.4	90.4
Whiteness, CIE, W	70.7	79.6	80.8	84.1
Light scattering coeff. (m ² /kg)	43.7	62.7	60.5	73.7
Opacity (%)	83.5	87.0	90.6	91.1

55

Similarly to what was shown in Example 5, the results here again show that PCC as filler and gypsum as coating pigment will give paper grades having particularly good optical properties. Note that in the experiments of the present example

- contrary to those of Ex. 5 - the papers do not contain any fluorescent whitening agent. Despite this fact the combination of PCC + gypsum produces a grade of paper with high degrees of brightness and whiteness. The use of this combination therefore may constitute a future method for the manufacture of paper and paperboard grades intended for use in contact with foodstuffs.

5

Example 7

Coating experiments in this example were carried out on wood-containing base paper having a basis weight of 49 g/m².

10

The base paper was manufactured with a pulp composition of 50/50 groundwood pulp/fully bleached pine sulfate. The groundwood pulp (Bure 80 EF from Bure träsleperi, Sweden) had a refining degree of 80 CSF.

Paper was produced with 11.3% PCC of the same type as in Example 6, on the experimental paper machine and under conditions similar to those described in the preceding example, but without any surface sizing.

15

Next, the wood-containing base paper was given a coating of the gypsum formulation described in Example 1, this coating being applied manually by means of a blade applicator (about 10.5 g of coating colour, dry basis, per m² applied on one side of the paper).

The optical properties mentioned above were determined; for results see Table 7.

Table 7

Brightness, % ISO	85.8
Whiteness CIE, W	71.4
Light scattering coeff. (m ² /kg)	83.9
Opacity (%)	90.0

25

These results show that it is possible to obtain good optical properties also on wood-containing coated paper, when PCC is used as filler and gypsum as coating pigment. This paper according to the invention has much higher degrees of brightness and whiteness than wood-containing coated papers that have been produced in a conventional manner; an example of such conventional paper grades being commercial LWC paper which will normally have a brightness value of between 70 and 75%ISO.

Claims

- 35 1. Process for manufacturing paper from a stock of pH >6.5, the preparation of the stock being effected with the use of cellulose fiber material containing 0.5 - 70% (w/w) of calcium sulfate (gypsum), in the form of coated paper with gypsum as coating pigment, and the gypsum-containing cellulose fiber material being made to form a suspension in an aqueous medium which is to form part of the stock, characterized in that
 - 40 (a) carbonate ions and/or hydrogen carbonate ions (CO₃²⁻ or resp. HCO₃⁻) are supplied to the aqueous medium, and
 - (b) the pH (at 25°C) in the aqueous medium is adjusted to above 7.3, with a preferred upper limit at pH 14, so that calcium carbonate precipitates and forms part of the suspension.
- 45 2. Process according to claim 1, characterized in that the paper produced is coated with a gypsum-containing coating color, the gypsum-containing cellulose fiber material being broke which is thus reused.
3. Process according to claim 1, characterized in that the cellulose fiber material is waste paper which contains gypsum.
- 50 4. Process according to any of claims 1-3, characterized in that for supplying carbonate and/or hydrogen carbonate ions a water-soluble carbonate salt and/or hydrogen carbonate salt is added, preferably one containing as its cation an alkali metal or ammonium ion.
- 55 5. Process according to claim 4, characterized in that the added carbonate and/or hydrogen carbonate amounts to more than 5% and less than 300% of the stoichiometric amount for forming calcium carbonate from the calcium sulfate present in the cellulose fiber material employed.

6. Process according to claim 4 or 5,
characterized in that the added carbonate and/or hydrogen carbonate amounts to more than 80% and less than
 200% of the stoichiometric amount for forming calcium carbonate from the calcium sulfate present in the cellulose
 fiber material employed.

5

7. Coated paper obtainable according to the process of any of claims 1 - 6.

8. Coated paper according to claim 7, containing filler in the base paper and pigment in a coating layer, wherein 5 -
 10 100% (w/w) of said filler consists of precipitated calcium carbonate (PCC), amounting preferably to 0,5 - 50% (w/w)
 of the weight of the paper, and 5 - 100% (w/w) of said pigment consists of gypsum.

9. Coated paper according to claim 8, wherein 5 - 60% of the filler of the base paper is precipitated calcium carbonate.

10. Coated paper according to any of claims 7 - 9, wherein the PCC in the base paper (w/w) is present in combination
 15 with a water-insoluble latex polymer having a glass transition temperature of < 50°C.

11. Coated paper according to any of claims 7 - 10, wherein the precipitated calcium carbonate is mainly a rhombohedral
 calcite.

20

Patentansprüche

1. Verfahren zur Herstellung von Papier aus einem Ganzstoff mit pH > 6,5, wobei die Herstellung des Ganzstoffes
 25 unter Verwendung von Cellulosefaser-Material, das 0,5 - 70% (Gew./Gew.) Calciumsulfat (Gips) enthält, in Form
 von beschichtetem Papier mit Gips als Beschichtungs-Pigment bewirkt wird und das Gips-haltige Cellulosefa-
 ser-Material veranlaßt wird, eine Suspension in einem wäßrigen Medium zu bilden, die einen Teil des Ganzstoffes
 bilden soll, dadurch gekennzeichnet, daß

30 (a) Carbonationen und/oder Hydrogencarbonationen (CO_3^{2-} bzw. HCO_3^-) dem wäßrigen Medium zugeführt
 werden und
 (b) der pH (bei 25°C) in dem wäßrigen Medium auf über 7,3 eingestellt wird, wobei eine bevorzugte Obergrenze
 bei pH 14 liegt, so daß Calciumcarbonat ausfällt und einen Teil der Suspension bildet.

35 2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das hergestellte Papier mit einer Gips-haltigen Beschich-
 tungsfarbe beschichtet wird, wobei das Gips-haltige Cellulosefaser-Material Fertigungsausschuß ist, der somit wie-
 derverwendet wird.

40 3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Cellulosefaser-Material Abfallpapier ist, das Gips
 enthält.

45 4. Verfahren nach irgendeinem der Ansprüche 1 - 3, dadurch gekennzeichnet, daß zwecks Zuführung von Carbonat-
 und/oder Hydrogencarbonationen ein wasserlösliches Carbonatsalz und/oder Hydrogencarbonatsalz zugesetzt
 wird, vorzugsweise eines, das als sein Kation ein Alkalimetall- oder Ammoniumion enthält.

50 5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß das zugesetzte Carbonat und/oder Hydrogencarbonat
 mehr als 5% und weniger als 300% der stöchiometrischen Menge zur Bildung von Calciumcarbonat aus dem in
 dem eingesetzten Cellulosefaser-Material vorhandenen Calciumsulfat beträgt.

6. Verfahren nach Anspruch 4 oder 5, dadurch gekennzeichnet, daß das zugesetzte Carbonat und/oder Hydrogen-
 carbonat mehr als 80% und weniger als 200% der stöchiometrischen Menge zur Bildung von Calciumcarbonat aus
 dem in dem eingesetzten Cellulosefaser-Material vorhandenen Calciumsulfat beträgt.

7. Beschichtetes Papier, erhältlich gemäß dem Verfahren von irgendeinem der Ansprüche 1 bis 6.

55 8. Beschichtetes Papier nach Anspruch 7, enthaltend Füllstoff in dem Rohpapier und Pigment in der Überzugsschicht,
 in welchem 5 - 100% (Gew./Gew.) des Füllstoffes aus gefälltem Calciumcarbonat (PCC) bestehen, wobei es vor-
 zugsweise in einer Menge von 0,5 - 50% (Gew./Gew.) des Gewichts des Papiers vorliegt, und 5 - 100% (Gew./Gew.)
 des Pigments aus Gips bestehen.

9. Beschichtetes Papier nach Anspruch 8, in welchem 5 - 60% des Füllstoffes des Rohpapiers aus gefälltem Calciumcarbonat bestehen.

5 10. Beschichtetes Papier nach irgendeinem der Ansprüche 7 - 9, in welchem das PCC in dem Rohpapier (Gew./Gew.) in Kombination mit einem wasserunlöslichen Latex-Polymer mit einer Glasübergangstemperatur von < 50°C vorhanden ist.

10 11. Beschichtetes Papier nach irgendeinem der Ansprüche 7 - 10, in welchem das gefällte Calciumcarbonat hauptsächlich ein rhomboedrischer Calcit ist.

Revendications

15 1. Procédé de fabrication de papier à partir d'une pâte à papier de pH supérieur à 6,5, la préparation de cette pâte de papier se faisant à l'aide d'une matière fibreuse de cellulose contenant 0,5-70% (p/p) de sulfate de calcium (gypse), sous forme de papier couché utilisant du gypse en tant que pigment de couchage, et la matière fibreuse de cellulose contenant du gypse étant réalisée de manière à former une suspension dans un milieu aqueux qui doit constituer une partie de la pâte à papier, ce procédé étant caractérisé par le fait que:

20 a) des ions carbonate et/ou des ions carbonate d'hydrogène (CO_3^{2-} ou, respectivement, HCO_3^-) sont alimentés dans le milieu aqueux, et
b) le pH (à 25° C) dans le milieu aqueux est ajusté au-dessus de 7,3, la limite supérieure privilégiée se situant au pH 14, de manière à ce que le carbonate de calcium précipite et constitue une partie de la suspension.

25 2. Procédé selon la revendication 1, caractérisé par le fait que le papier produit est couché avec une sauce de couchage contenant du gypse, la matière fibreuse de cellulose contenant du gypse étant constituée par des cassés de la fabrication qui sont ainsi réutilisés.

30 3. Procédé selon la revendication 1, caractérisé par le fait que la matière fibreuse de cellulose est constituée par des vieux papiers qui contiennent du gypse.

35 4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé par le fait que, pour apporter des ions carbonate et/ou des ions carbonate d'hydrogène, on ajoute un sel de carbonate et/ou un sel de carbonate d'hydrogène soluble dans l'eau, de préférence un sel contenant, en tant que cation, un métal alcalin ou un ion ammonium.

5. Procédé selon la revendication 4, caractérisé par le fait que le carbonate et/ou le carbonate d'hydrogène ajouté correspond à plus de 5% et moins de 300% de la quantité stoechiométrique nécessaire pour former le carbonate de calcium à partir du sulfate de calcium présent dans la matière fibreuse de cellulose utilisée.

40 6. Procédé selon l'une ou l'autre des revendications 4 ou 5, caractérisé par le fait que le carbonate et/ou le carbonate d'hydrogène ajouté correspond à plus de 80% et moins de 200% de la quantité stoechiométrique nécessaire pour former le carbonate de calcium à partir du sulfate de calcium présent dans la matière fibreuse de cellulose utilisée.

7. Papier couché pouvant être obtenu suivant le procédé selon l'une quelconque des revendications 1 à 6.

45 8. Papier couché selon la revendication 7, contenant des charges dans le papier support et un pigment dans une couche de couchage, caractérisé par le fait que 5-100% (p/p) desdites charges sont constituées par du carbonate de calcium précipité (CCP), équivalent de préférence à 0,5-50% (p/p) du poids du papier, et 5-100% (p/p) dudit pigment est constitué par du gypse.

50 9. Papier couché selon la revendication 8, caractérisé par le fait que 5-60% desdites charges du papier support sont constituées par du carbonate de calcium précipité.

10. Papier couché selon l'une quelconque des revendications 7 à 9, caractérisé par le fait que le carbonate de calcium précipité dans le papier support est présent (p/p) en combinaison avec un polymère de latex insoluble dans l'eau et ayant une température de transition vitreuse inférieure à 50° C.

55 11. Papier couché selon l'une quelconque des revendications 7 à 10, caractérisé par le fait que le carbonate de calcium

EP 0 457 822 B1

précipité qu'il contient est constitué principalement par un calcite rhomboédrique.

5

10

15

20

25

30

35

40

45

50

55